

Ozone as an oxidant for accelerated testing of pyrrhotite-induced concrete degradation

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Abstract

The iron-sulfide mineral pyrrhotite used in some home foundation construction is known to oxidize and form minerals deleterious to the concrete. Deterioration from this process can require decades to become apparent. The long timescale requires a method of accelerated aging to study the process and evaluate aggregate for use in concrete. We propose the use of ozone as an oxidant and present results of proof-of-concept experiments. Exposure of a thin mortar 'tile' to 500 ppb (ng/kg) ozone in air with 40 % humidity for 14 days tarnished some grains but did not otherwise show evidence of reaction. Exposure of a tile in a UV/Ozone cleaner with 70 % humidity and ozone concentration ranging from 40 to 50 ppm resulted in the growth of sulfate mineral encrustations on the surface and needle-like gypsum growth within the voids. Conceptually, the use of ozone avoids some complications associated with bleach submersion. Further study is needed to develop this potential method.

Keywords: *pyrrhotite, oxidation, ozone, mortar-bar test, concrete degradation*

1. INTRODUCTION

Pyrrhotite-bearing aggregate used in concrete has led to the degradation of residential foundations in an area of the Northeastern United States [1, 2]. The crushed-rock aggregate, identified from a quarry in CT, contains pyrrhotite. The iron in pyrrhotite oxidizes (and hydrates) in the presence of water and oxygen, additionally releasing hydrogen and sulfate ions. Volumetrically larger iron-containing phases (e.g., ferrihydrite, goethite) and sulfate-containing phases (e.g., monosulfate, ettringite, thaumasite) form by deposition or reaction with the cement paste. The resulting expansion leads to fractures damaging the foundation. This degradation process spans years, presenting a challenge for laboratory study of the mechanisms involved and for the use of cast mortar bars to test for potential reactivity [3]. Methods suggested for accelerating this process include elevated temperature, humidity, oxygen content, the addition of sodium hypochlorite (bleach), and/or the use of an electrochemical cell [4]. We propose using ozone to accelerate pyrrhotite oxidation as an alternative method for exploration, and present findings from proof-of-concept experiments. The accelerated mortar bar method of Rodrigues et al. involves twice-daily submersions in NaOCl solutions [3]. One challenge with the use of bleach is the growth of Friedel salts in the cement paste. Additionally, the potential inclusion of sodium at elevated levels in the cement paste can alter the behavior in the test [5]. A counterchallenge is the loss of elements to the bleach solution, including the sulfates in question. Exposing concrete to ozone in air would not involve these complications and would reflect the fact that damage seen in CT house foundations is often above grade, where the concrete would not be water saturated [6]. Ozone (O₃) has a higher oxidation potential (2.07 V) compared with hydrogen peroxide (H₂O₂) (1.77 V) or sodium hypochlorite (NaOCl, bleach) (1.4 V). As such, ozone can be a more effective oxidizing agent. Additionally, hydroxyl radicals (2.8 V) can be generated when ozone and water are present under ultraviolet radiation. Ozone has been shown to have an accelerating effect on the oxidative leaching of metals from sulfide ores [7, 8] and is likely applicable to the present problem. The mortar bar expansion test utilizes a geometry with a relatively low surface-

to-volume ratio. To maximize the exposure of pyrrhotite to ozone, the samples used here were cast as tiles and ground flat. Rather than expansion as an indicator of reactivity, we examine the surface for evidence of mineral modification and growth. In future work, X-ray diffraction (XRD) and X-ray fluorescence (XRF) will be utilized to monitor the growth of minerals as an indicator of oxidation and reactions within the cement paste.

2. EXPERIMENTAL PROGRAM

Mortar samples, both with and without pyrrhotite, were prepared according to ASTM C305. A nominally sulfide-free diabase aggregate, pyrrhotite (Wards Scientific – Galax, Virginia, USA, passing a 4.75 mm (#4), retained on 1.18 mm (#16) sieve), and Type I/II OPC were used. The mortar solids consisted of diabase sand (ASTM C33) in a 2.25 sand-to-cement ratio with 10 % pyrrhotite replacing diabase in pyrrhotite-bearing samples. The water-to-cement ratio was 0.5. Samples were molded in a 152 mm (6") x 152 mm (6") cube mold filled only to an approximate 6 mm depth. Samples were cured initially in a high-humidity chamber for 24 hours, and then for 14 days in a saturated lime-water bath. Samples were trimmed to ~ 100 mm x 100 mm flat "tiles" with one surface polished to 1200 grit to aid inspection (Figure 2.1). Following curing, samples were stored in an evacuated chamber at a pressure of 8.5×10^{-2} MPa until use.

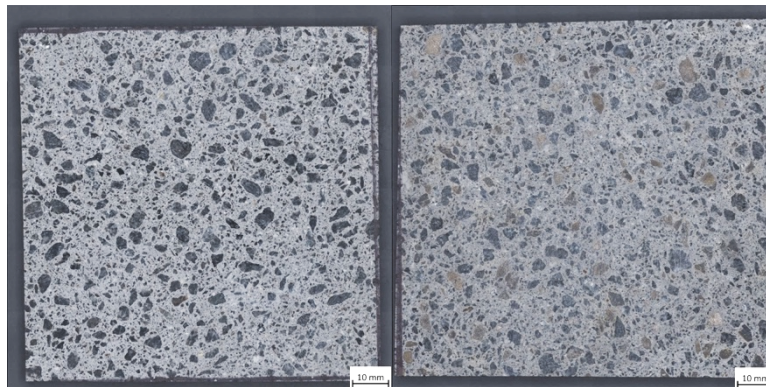


Figure 2.1: Pre-experiment mortar tiles. Left, control sample of diabase and OPC I/II cement. Right, 10 % of diabase sand replaced with natural pyrrhotite.

2.1 Controlled 500 ppb Ozone in Air

An initial experiment exposed one pyrrhotite and one control tile to ozone under a controlled atmosphere of 500 ppb (ng/kg) ozone in air (40 % humidity) for 14 days (Figure 2.1). During this time, one additional pyrrhotite-bearing tile was exposed to room conditions on a lab bench in case any effects of room air needed to be investigated.



Figure 2.1: Left, 500 ppb set-up. Right, UV/ozone cleaner set-up.

2.2 UV/Ozone Exposure

To investigate a more aggressive regimen, a pyrrhotite-bearing tile was placed in a UV/Ozone cleaner (Jelight Model No. 342) suspended over water with 90-minute exposure cycles twice daily for four days, followed by three days without exposure for four weeks (Figure 2.1). The size of this device

prevented the use of a pyrrhotite-free control sample. Relative humidity in the chamber was measured at 70 %. The water bath was monitored daily. In this type of device, atmospheric O_2 is exposed to UV radiation from a low-pressure mercury vapor grid lamp and converted to O_3 , while H_2O in the presence of both UV and O_3 can be converted to $OH^\cdot$. This type of device does not target a predetermined ozone concentration. Testing by the manufacturer gives a suggested range for our setup of 40–50 ppm ozone.

3. RESULTS

Following the completion of the two experiments, the samples were imaged, and sample the sample from the UV/Ozone experiment was studied using μ XRF. A 25 mm x 25 mm square was cut from each tile for analysis by scanning electron microscopy (SEM)/energy dispersive spectrometry (EDS). The remaining material from each sample was ground and homogenized for future XRD analysis.

3.1 Visual Observations

3.1.1 500 ppb Ozone Exposure

The pyrrhotite sample exposed to 500 ppb ozone showed visual signs of oxidation, characterized by a change in the surface color (bronzing) and sheen of the pyrrhotite. There were no ‘rust stains’ or other signs of oxidation at this concentration, for this duration. No change was noted in the control sample.

3.1.2 UV/Ozone Exposure

The pyrrhotite-bearing sample exposed in the UV/Ozone cleaner showed surface evidence of reaction, including “rust” stains around pyrrhotite grains, the appearance of fine white needle-like crystals in an air void exposed at the surface, and white crust spots on the surface. Analysis of needles at three weeks by micro-Raman (Bruker Senterra II) best match spectra collected from gypsum. SEM/EDS confirmed the presence of sulfur and calcium without other cations. (Figure 3.1).

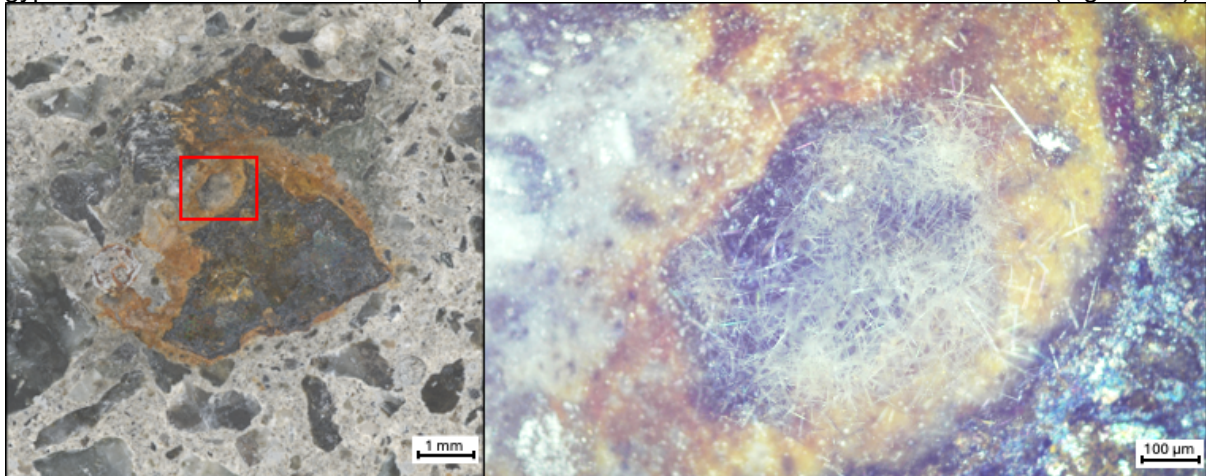


Figure 3.1: Sample P-2 (UV/ozone exposure) after three weeks. Left, staining and white mineral growth. Right, thin white needles can be seen growing into the cavity from the edges.

3.2 Analysis by μ XRF

The surface of the UV/Ozone exposure sample was examined by μ XRF (Bruker M4 Tornado^{plus}). μ XRF is a non-invasive technique that does not require sample preparation, allowing the sample to be fully analyzed later by other methods. Mapping sulfur distribution as shown in Figure 3.2 indicated a spread of sulfur from sulfide grains across and potentially into the cement paste.

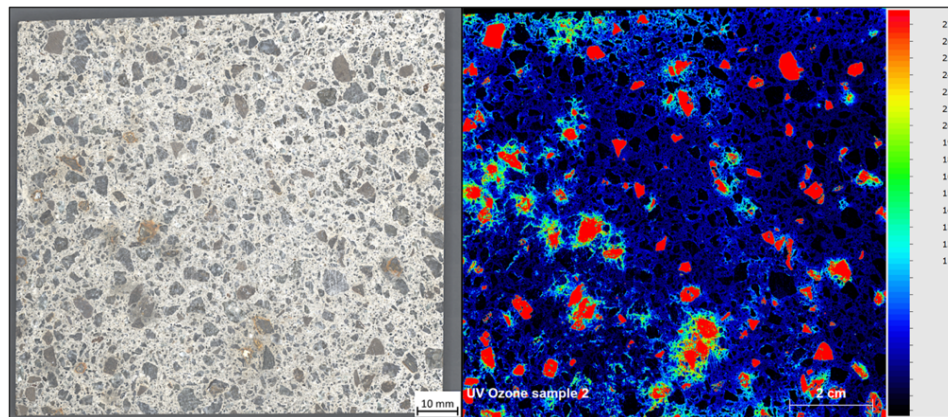


Figure 3.2: μ XRF 'Heat map' of sulfur abundance (EDS) in the UV/Ozone exposure sample showing sulfides (red), non-pyrrhotite aggregate (black), cement paste (blue), and areas of elevated sulfur within or upon the surface of the sample (light-blue, green, orange).

3.3 Analysis by SEM/Energy Dispersive Spectroscopy (EDS)

Retained sections of samples P-2 (UV/Ozone) and P-3 (500 ppb) were mounted on aluminum stubs and carbon-coated for analysis by SEM/EDS on a Tescan Mira4 field emission SEM with two Bruker XFlash 70 mm EDS detectors with 12 kV accelerating voltage and 5 nA beam current. Sample P-3 from the 500 ppb exposure experiments was examined and did not show significant mineral growth. Sample P-2, from the UV/Ozone exposure, showed the growth of mineral crusts over aggregate grains. The growths, as seen in Figure 3.3 (left, center), varied in chemistry across the grain, changing broadly in bands from the center, where potassium-calcium sulfates were found, through calcium sulfates amid patches of bare iron sulfide, and out onto the surface of the cement paste. This indicates a reaction between the sulfate ions and the cations in the cement or aggregate minerals. In other areas of P-2, needle-like growths are identified on the surface. They generally contain sulfur and calcium without other cations and are likely gypsum. The needles are surrounded by patches of thin growth on the surface (Figure 3.3, right).

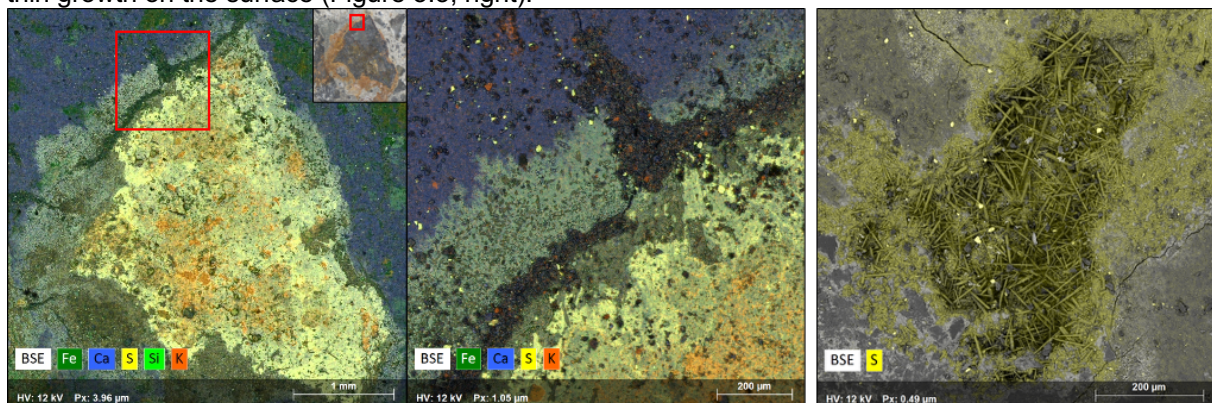


Figure 3.3: Sample surface after UV/ozone exposure. Left/Center, crust formed on an aggregate grain surface and cement paste. Inset, optical image. Others, SEM Backscatter Electron (BSE) image with EDS sulfur map overlay. Right, needle-like growth of minerals in a cavity at another spot.

4. DISCUSSION

The two methods of this study showed different levels of oxidation, as would be expected at different concentrations of ozone. The mineral crust formed is an indicator of early oxidation and reaction. Further testing by XRD and bulk XRF will help determine the extent of mineral alteration, and analysis of cross sections by EDS/SEM will help evaluate the depth of any alteration. In general, the ozone method addresses some criticisms of other acceleration methods by avoiding the addition of elements to the concrete as well as the loss of elements from it, due to the submersion bath. Furthermore, it more accurately recreates the conditions of aqueous chemistry that occur within the concrete pore structure of foundation walls. Oxidation in this test did not proceed to the point of fracturing, and not

all sulfide grains showed new mineralization indicative of oxidation and reaction. These tests show the basic feasibility of using ozone in this manner. Significant work would be required to develop this into a functional test for aggregate reactivity in concrete.

4.1 Future Work

- Reactions are limited by the diffusion of ozone through the mortar, potentially preventing the core of the sample from experiencing the full oxidizing effect. Further minimizing the thickness of sample would minimize this effect.
- Another approach to aid in ozone penetration of the sample would be to force humidified ozone/air through a sample under pressure. A flow-through system would significantly increase the cross-section of the sample exposed and continually renew the ozone that has been consumed.
- In this study, natural pyrrhotite was used, which complicates the interpretation of the results. In future studies, lab-produced pyrrhotite should be used to replace a portion of the aggregate, or a model aggregate containing pyrrhotite may be used [9].

We would like to acknowledge and thank Jana Butman of NIST for her assistance in conducting the 500 ppb experiment and discussions about ozone exposure of materials.

5. DISCLAIMER

Certain equipment, instruments, software, or materials, commercial or non-commercial, are identified in this paper in order to specify the experimental procedure adequately. Such identification does not imply recommendation or endorsement of any product or service by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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